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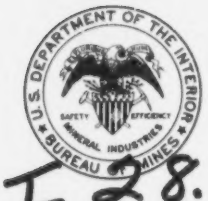
Wear Properties of Electrodeposited Titanium Diboride Coatings

By D. R. Flinn, J. A. Kirk, M. J. Lynch,
and B. G. Van Stratum



UNITED STATES DEPARTMENT OF THE INTERIOR

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Report of Investigations 8537

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary
BUREAU OF MINES

This publication has been cataloged as follows:

Wear properties of electrodeposited titanium diboride coatings.

(Bureau of Mines report of Investigations ; 8537)

Bibliography: p. 30.

Supt. of Docs. I 28.23:8537.

1. Protective coatings–Testing. 2. Titanium diboride–Electrometallurgy. 3. Mechanical wear. I. Flinn, David R. II. Series: United States. Bureau of Mines. Report of investigations ; 8537.

TN23.U43 [TA418.76] 622s [671.7'32] 80-606856 AACR1

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WEAR PROPERTIES OF ELECTRODEPOSITED TITANIUM DIBORIDE COATINGS

by

D. R. Flinn,[1] J. A. Kirk,[2] M. J. Lynch,[3] and B. G. Van Stratum[4]

ABSTRACT

A newly developed chemical conditioning techaique, which greatly simplifies the preparation of plating baths for the electrodeposition of titanium diboride (TiB_2) coatings, is described in this report. The new plating technique was used to prepare samples of titanium diboride (TiB_2) coatings on three types of substrate materials. These samples were then evaluated in both low- and high-speed wear-test programs to determine the wear resistance, microhardness, and adhesion of the coatings. In general, it was found that the wear resistance of the coatings is independent of substrate. Scanning electron micrographs have shown that the coating wear surfaces are very smooth, suggesting slow and continuous removal of the coating during the wear test (that is, adhesive wear). Adhesion between the coating and all substrates was excellent. Microhardness results show that the TiB_2 coating is harder than alumina, with a hardness value exceeding 5,000 kg/mm^2 measured in one test. The results of the wear tests show that TiB_2 coatings have relatively poor wear resistance compared with alumina in low-speed unlubricated sliding environments, but exhibit wear properties comparable with alumina in high-speed unlubricated sliding environments.

INTRODUCTION

The U.S. Department of the Interior, Bureau of Mines, has developed techniques to electrodeposit erosion- and corrosion-resistant coatings of titanium diboride (TiB_2) in order to reduce the requirements for strategic and critical materials such as nickel, chromium, and cobalt currently used in applications where material loss caused by wear is a significant problem. Titanium

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diboride shows a reasonable potential for such applications as a wear-resistant hard facing for valve components for use in erosive and abrasive environments such as coal gasification systems, as a coating on high-speed cutting tools and drill bits, and as a coating on many different types of bearing surfaces.

In previous reports (2, 5)[5] techniques to prepare adherent, erosion-resistant coatings of TiB_2 are described. These techniques, along with an improved bath preparation procedure which is described in this report, were used to prepare the TiB_2 coatings evaluated in the present study. These previous studies (2, 5) showed that TiB_2 coatings prepared by electrodeposition offer advantages compared with other preparative methods, such as chemical vapor deposition, since very adherent deposits are readily produced on virtually any shape object.

Journal bearings, pistons in engine cylinders, metal cutting tools, and some electrical contacts are but a few of the huge number of situations where wear occurs owing to sliding contact between two materials. In the majority of cases of sliding contact, loss of material occurs owing to adhesive or abrasive wear (4). In one of the previous reports (5), it was shown that electrodeposited TiB_2 coatings can be prepared that are highly resistant to material loss during impingement of high-velocity alumina and silicon carbide powders. Because of this observed erosion resistance and the known nigh melting point and hardness of TiB_2, it was felt that this material also might exhibit low sliding wear rates since these properties are known to influence the mechanism of wear (4, 7).

For these reasons, a program was initiated to study the sliding wear properties of TiB_2 electrodeposited coatings. Low- and high-speed pin-on-disk wear tests, under dry and lubricated conditions, were run to determine the wear rates. Because TiB_2 is readily deposited on molybdenum, nickel, and Inconel,[6] these materials were chosen as substrates to be coated for the sliding wear tests. Tests were conducted using TiB_2 in sliding contact with other TiB_2 coatings and with a hardened steel surface. For comparison, uncoated substrate samples were tested. Since alumina is a widely used and well characterized, very hard, wear-resistant material (1, 6), Al_2O_3 samples were also included in this study. Owing to the similar physical properties of TiB_2 and Al_2O_3, it was felt that this comparison was of importance. The ease of preparation of TiB_2-coated shapes compared with that of shapes of Al_2O_3 single crystals could result in the use of TiB_2 coatings both to substitute for Al_2O_3 and in other applications where wear resistance is desirable.

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[5]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[6]Reference to specific trade names is intended for identification purposes only and does not imply endorsement by the Bureau of Mines.

EXPERIMENTAL METHOD

Plating Electrolyte Preparation

A new method was devised that permitted the preparation of stable plating electrolytes in much less time than is required using the earlier methods (2, 5). The composition of the electrolyte was similar to that used in the earlier studies. The initial constituents, in weight-percent, were $LiBO_2$, 58.41; $NaBO_2$, 38.95, Li_2TiO_3, 0.76; NA_2TiO_3, 0.99; TiO_2, 0.55; Ti (as sponge) 0.34. The total titanium content was 1.33 wt-pct. In one bath, a titanium content of twice this amount was investigated. These electrolyte components were converted to the anhydrous state prior to weighing and mixing. The Li_2TiO_3, Na_2TiO_3, and TiO_2 were dried in a vacuum oven at 300° C for 6 hours. The weight change of the salts was less than 1 pct. The $LiBO_2$ and $NaBO_2$, which contain two and four waters of hydration, respectively, were dried separately in vacuum ovens with the temperature slowly raised from 100° C to 320° C over a period of 5 days. This removed 99 pct of the water, which was collected in liquid-nitrogen-cooled traps. The dried $LiBO_2$ and $NaBO_2$ were then fused separately at 900° C and 1,000° C, respectively, in platinum crucibles for 2 hours under a flow of argon to remove the last traces of water.

In the earlier work (2, 5), molten plating baths were "conditioned" at 900° C through an electrochemical process by means of a constant current passed between a TiB_2 anode and a nickel or Inconel cathode, with the desired reaction probably occurring at or near the cathode surface. This conditioning involved several successive periods lasting a total of 6 to 14 hours of plating time for the 1.6-kg baths and 20 to 25 hours for the 6.5-kg baths. A new, less time-consuming, and more efficient method of bath conditioning has been devised. Previous spectroscopic investigations (2) at the Oak Ridge National Laboratory revealed that Ti^{3+} was the most abundant titanium species in a molten lithium- and sodium-metaborate mixtere that contained a mixture of TiO_2 and metallic titanium. This led to a chemical conditioning procedure based on the following reaction:

$$3Ti^{4+} + Ti = 4Ti^{3+} \qquad (1)$$

Titanium metal in the form of a metal sponge was selected owing to its large surface area. The titanium metal reduces the Ti^{4+} species in the bath (TiO_2, Li_2TiO_3, and Na_2TiO_3) to Ti^{3+} by a chemical means. This chemical conditioning procedure produces an electrolyte from which good TiB_2 deposits may be deposited immediately after the electrolyte components have been thoroughly mixed.

To chemically produce a "conditioned" electrolyte, that is, an electrolyte from which quality TiB_2 coatings could be deposited, it is desirable to produce the active Ti^{3+} species in the presence of a minimum of sodium-containing components to avoid the possibility of the formation of sodium metal. The $LiBO_2$, Li_2TiO_3, and Na_2TiO_3 along with the TiO_2 and Ti sponge are heated to 900° C in an argon atmosphere, then stirred for 2 hours and cooled. The $NaBO_2$ is then added, and the mixture heated to 900° C in argon and again stirred for 2 hours. The conditioned bath is then ready to give efficient TiB_2 deposits. Coatings were electrodeposited in plating cells of the type

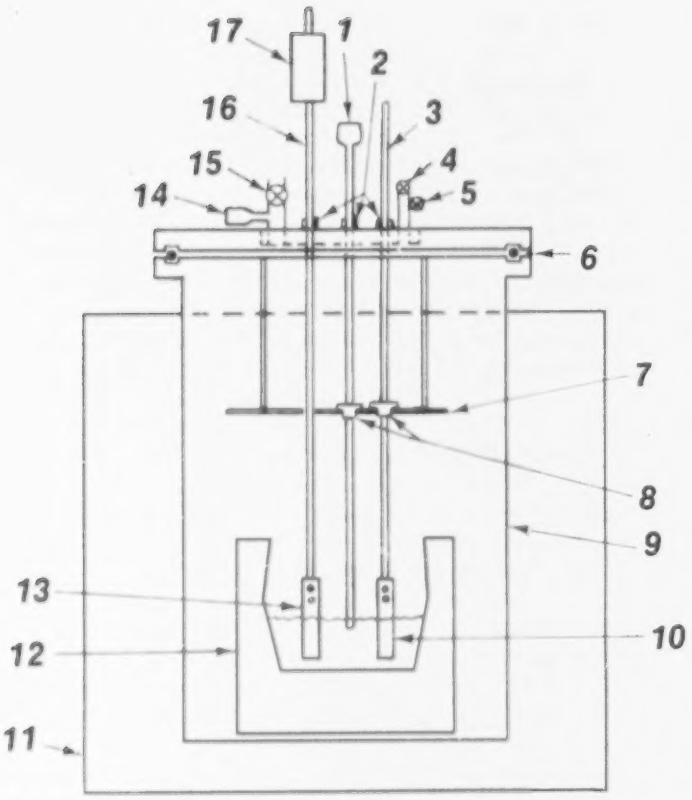

FIGURE 1. - Diagram of TiB_2 plating cell: (1) Thermocouple, (2) Teflon O-ring fittings, (3) anode holder, (4) vacuum line, (5) argon inlet, (6) O-ring seal, (7) heat shield, (8) boron nitride insulators, (9) Inconel 600 pot, (10) TiB_2 anode, (11) resistance-heated furnace, (12) Inconel 600 cell, (13) cathode, (14) vacuum gage, (15) argon outlet, (16) cathode holder, (17) mercury or graphite brush contactor.

shown in figure 1. Prior to each deposit the cell was evacuated and slowly heated to 600° C with the pressure not allowed to rise above 20 Pa (~0.15 torr). At 600° C, when the pressure dropped below 13 Pa (~0.1 torr), argon was introduced, and the cell was then heated to 900° C under a flow of argon. A stirrer was then lowered into the molten electrolyte and the bath stirred. Next, the electrodes were lowered into the electrolyte, and the electrolysis current was started immediately. Generally, the cathode was rotated while the TiB_2 anode was held stationary. A rotating graphite contactor was used to provide electrical contact to the rotating cathode. During electrodeposition, the cell current was kept constant and time was recorded to determine the charge passed during deposition. The applied potential was also recorded.

Containers for the electrodeposition electrolyte were made from a single piece of 1.6-mm Inconel 600 sheet. Two container sizes were used. The smaller size was 12.0 cm in diameter and 12.5 cm high and contained a 7.6-cm depth of electrolyte weighing approximately 1.6 kg. The larger containers were 17.2 cm in diameter and 17.8 cm high and were filled to a depth of 11.4 cm with 5.6 kg of electrolyte. A titanium crucible of size similar to the smaller Inconel crucible was used also.

Nickel, Inconel, and molybdenum were used as cathode materials. Substrate surface preparation procedures are described later. Anodes were hot-pressed TiB_2 that were initially 1.25 cm by 2.4 cm by ≈ 15 cm in length.

Representative deposits were examined by such techniques as X-ray diffraction, scanning electron microscopy, and Auger electron- and proton-induced X-ray emission spectroscopies to determine coating purity, roughness, and crystal orientation.

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Wear Testing Apparatus

To evaluate the wear behavior of TiB_2 coatings, two types of wear testing machines were used. One machine was a conventional pin-on-disk wear-test apparatus of the type described by Rabinowicz (4). Figure 2 is a photograph of this machine. The conventional pin-on-disk apparatus is composed of a loading arm (fig. 2) that contains a strain ring and a platform that can rotate at variable speed. The 0.64-cm-diameter wear test pin mounts in a cylindrical holder at the end of the loading arm, and the disk is clamped to the platform. Normal loads (typically less than 1 kg) are applied in the form of dead weights directly over the pin, and the resultant friction force is measured by the strain ring and a suitable strip chart recorder. This conventional pin-on-disk apparatus was used for wear testing for surface speeds under 6 m/min (~20 ft/min).

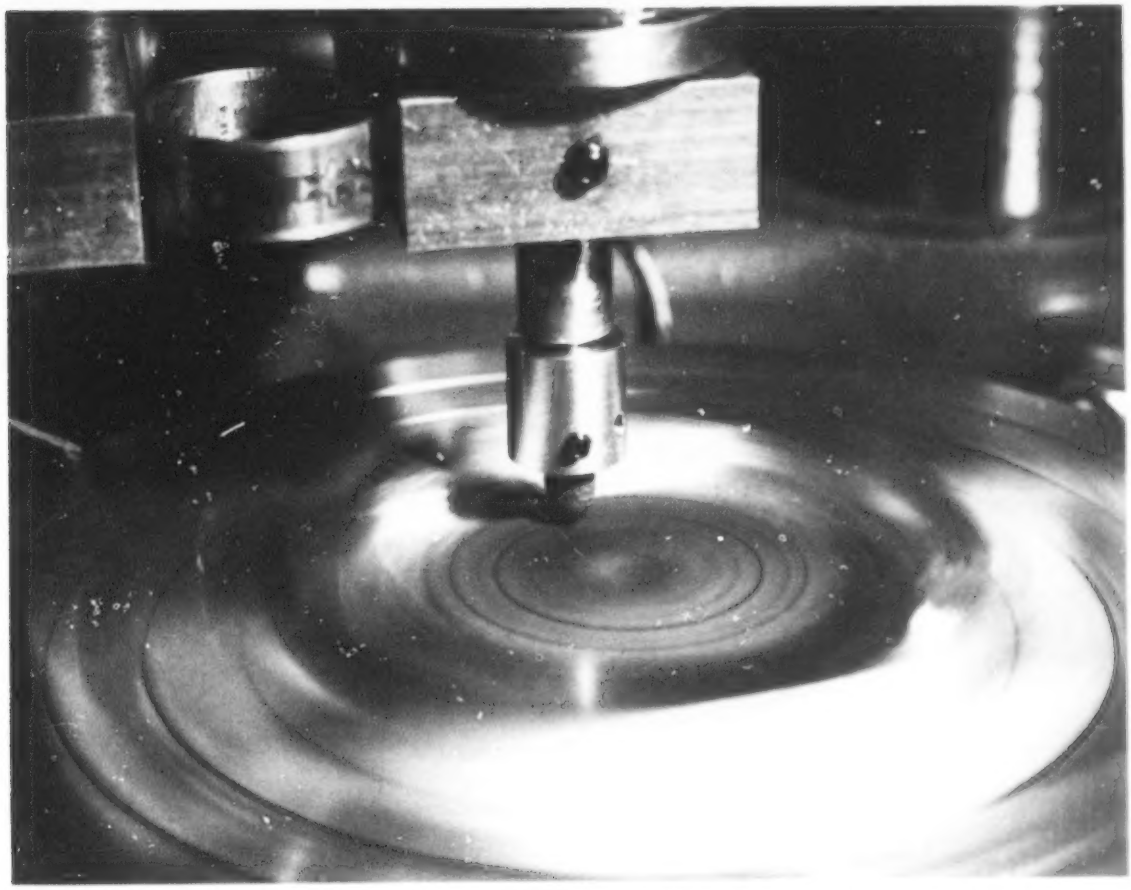


FIGURE 2. - Pin-on-disk apparatus used to determine the low-speed wear properties of TiB_2-coated materials. In test shown here, a molybdenum pin coated with TiB_2 is subjected to wear against a rotating TiB_2-coated molybdenum sheet. The coefficient of friction is measured by the force ring shown in the upper left of the picture.

The second type of wear-test machine used was a modified pin-on-disk machine. For this apparatus, a 2.54-cm-thick disk, 20.3 cm in diameter, was mounted in place of a grinding wheel on the spindle of a surface grinding machine. The disk was SAE 4150 steel hardened to R_c52. The same loading arm described for the conventional pin-on-disk machine was used for this machine, so that rubbing occurred between the circumference of the steel wheel and the wear-test pins. Typically, the modified pin-on-disk machine was used at surface speeds of ~1,800 m/min (~6,000 ft/min), with normal loads less than 1 kg. During a lubricated high-speed wear test, the entire contact region between the pin and steel wheel was flooded with nonrecirculating SAE 30 oil.

Wear-Test Pins and Wear Evaluation

The 0.64-cm-diameter pins used in both wear-test machines were cut to a 1.91-cm length. This size was selected so that pins could conveniently be observed in the scanning electron microscope. The TiB_2-coated end of the rod had the hemispherical tip with a 0.32-cm (1/8-inch) radius. The exact radius of the coated hemispherical end (R_o) was determined by using an optical comparator.

To compute the volume of TiB_2 material removed in the wear test, the diameter of the wear flat (on the pin) was determined by using an optical microscope. Using the notation given in figure 3, and assuming that the volume removed is that of a segment of a sphere of radius R_o, the volume of wear was determined from the equations:

$$V = \pi R_o^3 \left[\frac{2}{3} - \frac{Z_o}{R_o} + \frac{1}{3} \left(\frac{Z_o}{R_o} \right)^3 \right] \tag{1}$$

where $$Z_o^2 = R_o^2 - \left(\frac{d}{2} \right)^2 \tag{2}$$

V = volume of removed material

d = diameter of wear flat (assumed to be circular)

R_o = radius of coated hemispherical tip

$$Z_o = \sqrt{R_o^2 - \left(\frac{d}{2} \right)^2} = R_o - h$$

h = height of spherical segment removed

Other symbols shown in figure 3 will be introduced later.

The wear rate (WR) of the pin for each pin-and-disk combination was computed from the equation

$$WR = \frac{V}{XL}, \tag{3}$$

where WR = wear rate (mm^3/kg-km)

X = total sliding distance in wear test (km)

L = normal load on pin (kg)

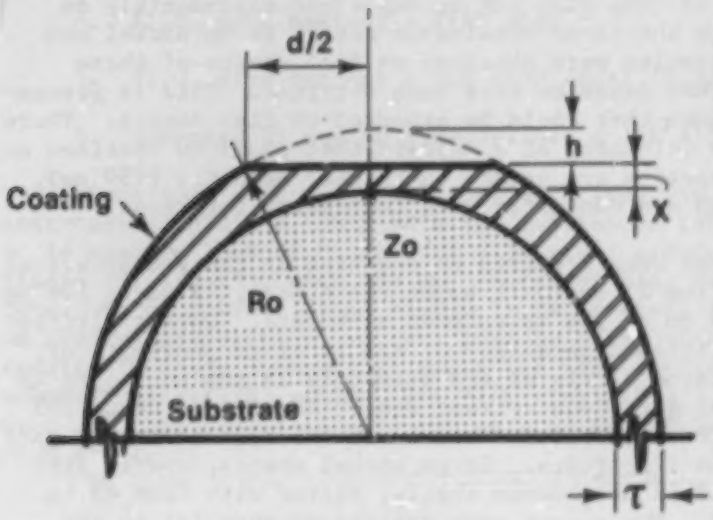
The units selected for the wear volume (mm^3) and for the wear rate $\frac{(mm^3)}{kg\text{-}km}$ of TiB_2 appear frequently in the literature when evaluating the wear of Al_2O_3 against steel. Since the wear measured during the tests conducted for this investigation were compared with those of Al_2O_3 (1, 6), the wear rate units mentioned above were used.

Other Test Equipment

To further investigate the wear behavior of the TiB_2-coated pins, scanning electron microscope (SEM) pictures were taken before and after wear testing. Selected photomicrographs are discussed in the section on SEM results. In addition, a Tukon microhardness tester was used to evaluate the indentation hardness of TiB_2 coatings. In a typical case the indentations were taken on a wear flat at the smoothest location possible (flats are approximately 0.10 cm in diameter). These tests will be discussed in more detail in the section on microhardness results.

Substrate Preparation

Coatings of TiB_2 were electrodeposited on hemispherically tipped pins of molybdenum, nickel, and Inconel, 0.6 cm in diameter, and on 5.1-cm by 5.1-cm sheets of molybdenum and nickel, which were 0.079 cm and 0.6 cm thick, respectively.



WORN PIN SECTION

FIGURE 3. - Minimum coating thickness calculation.

All substrates were preheated by grinding with progressively finer silicon carbide paper from 240 to 600 grit, washed in distilled water, degreased in trichloroethylene, etched in the appropriate etching solution, again washed in distilled water, and finally degreased in trichloroethylene. The nickel and Inconel substrates were etched in 10 vol-pct HNO_3 at 70° C for 5 and 30 minutes, respectively. Molybdenum substrates were etched in a fresh solution consisting of 6 g $K_3Fe(CN)_6$ and 1 g NaOH in 200 g water for 20 minutes and then rinsed in 10 vol-pct HCl for 3 minutes.

EXPERIMENTAL RESULTS AND DISCUSSION

Electrolyte Conditioning

The new chemical conditioning procedure resulted in greatly reducing the time required to prepare an electrolyte from which hard, consolidated coatings of TiB_2 could be electrodeposited at high current efficiency. Previous electrolyte preparations required a lengthly electrochemical conditioning period, where about 10^5 coulombs of charge (approximately 1 faraday) was passed over a 6- to 14-hour period for the smaller 1.6-kg electrolyte before consolidated coatings of TiB_2 could be obtained with good efficiency. The new chemical conditioning method forms the active electrolyte during the 4-hour mixing period. In an electrochemically conditioned electrolyte, using a rotating nickel cathode and a TiB_2 anode and an average cathode current density of 79.0 ma/cm^2, the average current efficiency was 10.4 pct during the first 15 hours. In the chemically conditioned bath the current efficiency for the first coating was 53.7 pct, with a cathode current density of 104 ma/cm^2, and the average for the first 15.5 hours was 52.7 pct with an average cathode current density of 122 ma/cm^2. After the electrolytes were conditioned, the cathode current efficiencies were essentially the same.

TiB_2-Coated Specimens

The coatings on nickel and Inconel were generally very smooth. This is thought to be due to a large difference in the thermal expansion of these materials with respect to the TiB_2 coating. In the case of nickel and Inconel, as the sample cools to room temperature following the electrodeposition of the coating, the outer portion of the TiB_2 coating flakes off, leaving a smooth surface. This remaining coating, however, is extremely adherent and resistant to spalling. In the case of small-diameter rods, this limits the maximum thickness of TiB_2 that can be deposited reproducibly on these materials. This maximum thickness obtainable was 71 μm on nickel and 104 μm on Inconel. Similar results were obtained on flat sheets of these materials, although much thicker deposits have been obtained. This is presumably due to the smaller stresses that would be expected on flat sheets. There appears to be no limit to the thickness of a deposit that could be obtained on molybdenum; however, while deposits are smooth on thinner deposits (<50 μm), they become increasingly rough and dendritic with increasing thickness.

Titanium diboride coatings were prepared on the tips of the hemispherical pins to thicknesses ranging from 25 μm to 71 μm on the nickel, 23 μm to 104 μm on the Inconel, and 74 to 234 μm on the molybdenum substrate. During electrodeposition, the pins were positioned parallel to, and in close proximity of, the anode. The pins were rotated slowly at approximately 25 rpm to insure an evenly distributed coating using cathode current densities of from 64 to 195 ma/cm^2. A large Inconel stirrer was rotated slowly in the bath to insure good mass transport to and from the electrodes. Seven nickel sheets, coated with from 18 to 102 μm of TiB_2, and 12 molybdenum sheets, coated with from 43 to 188 μm of TiB_2, were prepared. The sheets were positioned parallel to the anode during preparation of the coating to insure an evenly distributed deposit, and cathode current densities of 64 to 155 ma/cm^2 were used.

Low-Speed Wear

Table 1 is a summary of the low-speed wear tests conducted for this investigation. The column headings at the top of the table are self-explanatory with the exception of contact pressure and sequential (SEQ) test. Contact pressures were obtained at the end of the wear test by dividing the wear flat area into the normal load. The purpose of this number (contact pressure) is to provide a value of the normal stresses under the pin and to compare the end result of one wear test with that of another. The entries for SEQ test refer to tests run on the same pin and are indicated by an S in the SEQ test column. Several of the SEQ tests (for example, 3C to 3H) were interrupted during the test, and the pins were observed in the SEM. The pin was then replaced in the loading arm (identical in position to its previous orientation), and the wear test was continued. For SEQ tests, wear rates were computed for the same test number (for example, 3C to 3H) by taking the total volume of material removed (at that point in the test) and dividing by the normal load and the total distance slid. The "time of test" values for these tests are the times between sequential observations. Contact pressures were calculated by dividing the normal load by the wear flat area at that point in the test. SEM micrographs of selected sequential observations are discussed in a later section on SEM results.

The pattern of the wear testing in table 1 can be grouped into the following categories:

1. TiB_2 pins against TiB_2 disks.
2. TiB_2 pins against a SAE 4150 steel (R_c52) disk.
3. Steel ball bearing pins against a TiB_2 disk.
4. Al_2O_3 pins against a TiB_2 disk.
5. Al_2O_3 pins against a SAE 4150 steel (R_c52) disk.
6. Uncoated Ni and Mo pins against a SAE 4150 steel (R_c52) disk.

Since much of the initial work with TiB_2 was used to find appropriate wear-test conditions, only selected entries in table 1 will be discussed. If it is assumed that Al_2O_3 against 4150 steel provides a suitable baseline (tests 13, 14, 15), then the wear rates of TiB_2 can be compared to this baseline. Note, however, that Al_2O_3 single crystals show a wear rate that depends on crystal orientation, so care must be taken with this comparison. The results in table 1 show that among the TiB_2 coatings, one, on a molybdenum substrate (test 7B) against SAE 4150 steel (R_c52), gave the lowest wear rate. Even so, this combination is not as good as single crystals Al_2O_3 against SAE 4150 steel.

TABLE 1. - Low-speed pin-on-disk tests[1]

Test	Pin[2]	Disk[2]	SEQ test[3]	Wear rate, $mm^3/kg\text{-}km$	Friction coefficient,[4] μ	Speed, m/min	Load, g	Time of test, min:sec	Contact pressure, kg/mm^2
1B	TiB_2 on Ni (HC-298).	TiB_2 on Ni (HC-294)		41.3	ND	21.8	200	1:20	6.52×10^{-2}
2B	TiB_2 on Mo (HC-300).	TiB_2 on Mo (HC-299)		536	ND	2.19	50	1:15	3.02×10^{-2}
3C	TiB_2 on Mo (HC-302).	4150 steel (R_c~52).	S	9.467×10^{-1}	0.16, 0.40	2.54	500	55:24	3.26×10^{-1}
3D	.....do.....	.....do.....	S	9.8×10^{-1}	.17, .50	2.54	500	90:00	1.96×10^{-1}
3E	.....do.....	.....do.....	S	9.8×10^{-1}	.17, .50	2.54	500	90:00	1.96×10^{-1}
3F	.....do.....	.....do.....	S	2.85×10^{-1}	0.44	2.57	500	120:00	3.89×10^{-1}
3G	.....do.....	.....do.....	S	2.85×10^{-1}	.44	2.57	500	120:00	3.89×10^{-1}
3H	.....do.....	.....do.....	S	6.99×10^{-1}	.28	2.80	500	751:15	3.01×10^{-1}
4B	TiB_2 on Ni (HC-303).	.....do.....		114	.16, .56	1.77	500	55:25	2.24×10^{-1}
5B	TiB_2 on Ni (HC-304).	.....do.....	S	ND	.52	2.57	500	120:00	ND
5C	.....do.....	.....do.....	S	1.01×10^{-1}	.36	2.70	500	750:04	7.70×10^{-1}
7B	TiB_2 on Mo (HC-313).	.....do.....		8.39×10^{-2}	.40	3.04	500	1,023:36	6.69×10^{-1}
8	Steel ball bearing..	TiB_2 on Mo (HC-299)		708	.64	2.13	50	9:20	8.06×10^{-2}
9	.....do.....	.....do.....		1,460	ND	2.26	50	9:20	5.22×10^{-2}
10	Al_2O_3 single crystal	.....do.....		7,360	ND	2.26	50	9:21	6.59×10^{-2}
11	.....do.....	.....do.....		5,250	.48	1.92	50	9:20	8.39×10^{-2}
12	Steel ball bearing..	4150 steel (R_c~52).		8.3	.16	2.01	500	55:24	1.01
13	Al_2O_3 single crystal	.....do.....		<.001	.16	2.50	500	55:24	ND
14	.....do.....	.....do.....		[5]18.1×10^{-3}	.50	2.30	650	ND	1.33
15	.....do.....	.....do.....		[5]$.15 \times 10^{-3}$	.69	2.30	650	ND	14.60
16B	Ni.....	.....do.....		2.39×10^{-1}	.68	2.77	500	25:00	8.71×10^{-1}
17B	Ni.....	.....do.....		2.55×10^{-1}	.68	2.77	500	68:52	5.10×10^{-1}
18B	Mo.....	.....do.....		1.33×10^{-2}	.24	2.77	500	43:43	2.80
19B	Mo.....	.....do.....		9.10×10^{-3}	.28	2.69	500	75:33	2.61

ND Not determined.

[1]Orientation of pin was random except for test 10, where $\theta = 0$, α-axis direction, and for tests 11 and 13, where α-axis was along normal [0001] direction.

[2]Individual coatings are labeled "HC-".

[3]S indicates a sequential test.

[4]Where 2 numbers are listed, test started at the lower value and within 5 minutes went to the higher, final value.

[5]Typical low-speed value from the literature.

In some cases the wear rate of the uncoated substrate was similar to that of the coated pins. In order to compare the results obtained with the various pin-on-disk combinations, two summary tables of the data from table 1 are shown. Table 2 gives a comparison of the low-speed wear results for various pins where TiB_2 coatings were used as the disk. These results suggest that TiB_2 coatings (on Mo or Ni) provide superior wear resistance when sliding against other TiB_2 coatings.

TABLE 2. - Summary of low-speed wear-test results with TiB_2-coated disks

Test	Pin[1]	Disk[1]	Wear rate, $mm^3/kg-km$
1B	TiB_2 on Ni (HC-298).	TiB_2 on Ni (HC-294)	41.3
2B	TiB_2 on Mo (HC-300).	TiB_2 on Mo (HC-299)	536
8	Steel ball bearing..	.....do.....	708
9	.....do.....	.....do.....	1,460
10	Al_2O_3 single crystal	.....do.....	7,360
11	.....do.....	.....do.....	5,250

[1]Individual coatings are labeled "HC-".

Wear rates of selected TiB_2 coatings and other materials used as pins against a 4150 steel disk (hardened to R_c~52) are compared in table 3. The TiB_2 coatings on nickel and molybdenum have approximately the same wear rate. (Note: wear rate differences of factors of 2 to 4 are not considered significant.) These coatings are more wear resistant than the steel ball bearing, but less wear resistant, by at least one order of magnitude, than the Al_2O_3 single crystal. In addition, it appears that the substrates by themselves are as good or even better than the combination of coating and substrate. It is not clear at this time why this should be. From the results shown in tables 1 to 3, it can be concluded that TiB_2-coated molybdenum or nickel specimens offer no advantage over other hard materials in low-speed sliding wear applications.

TABLE 3. - Summary of low-speed wear-test results with steel disks

(Disks, 4150 steel, R_c~52)

Test	Pin[1]	Wear rate, $mm^3/kg-km$
3F	TiB_2 on Mo (HC-302)...	2.85×10^{-1}
5C	TiB_2 on Ni (HC-304)...	1.01×10^{-1}
7B	TiB_2 on Mo (HC-313)...	8.39×10^{-2}
12	Steel ball bearing....	8.32
13	Al_2O_3 single crystal..	<.001
16B	Ni.....	2.39×10^{-1}
18B	Mo.....	1.33×10^{-2}

[1]Individual coatings are labeled "HC-".

High-Speed Wear

Table 4 is a summary of high-speed (tests run on the modified pin-on-disk machine at ~1,800 m/min) wear tests. There are six interrupted wear tests listed in table 4 (tests 20, 22, 25, 26, 28, 30), one for each of the three substrates (Mo, Ni, Inconel) under both lubricated and unlubricated test conditions.

TABLE 4. - High-speed pin-on-disk tests[1-3]

Test[4]	Pin[5]	SEQ Test[6]	Wear rate, $mm^3/kg-km$	Friction coefficient, μ	Load, g	Time of test, min:sec	Contact pressure, kg/mm^2
20B	TiB_2 on Ni (HC-307)....	S	3.83×10^{-2}	0.18	200	1:01	2.60×10^{-1}
20C	.....do.....	S	3.72×10^{-2}	.18	200	:59.6	1.88×10^{-1}
21B	TiB_2 on Ni. (HC-309)...		1.14×10^{-2}	.15	200	2:00	3.33×10^{-1}
+22B	TiB_2 on Ni (HC-312)....	S	1.37×10^{-3}	.06	500	5:00	9.60×10^{-1}
+22C	.....do.....	S	2.20×10^{-3}	.03	500	10:45	4.28×10^{-1}
+23B	TiB_2 on Ni (HC-350)....		4.59×10^{-4}	.03	500	15:31	9.60×10^{-1}
24B	TiB_2 on Mo (HC-332)....		1.41×10^{-2}	.13	200	2:20	2.94×10^{-1}
25B	TiB_2 on Mo (HC-336)....	S	2.48×10^{-2}	.15	200	1:01	3.37×10^{-1}
25C	.....do.....	S	1.67×10^{-2}	.18	200	6:04	1.56×10^{-1}
25D	.....do.....	S	1.52×10^{-2}	.18	200	8:19	1.11×10^{-1}
+26B	TiB_2 on Mo (HC-338)....	S	2.18×10^{-3}	.04	500	4:29	8.54×10^{-1}
+26C	.....do.....	S	1.73×10^{-2}	.03	500	11:00	5.17×10^{-1}
+27B	TiB_2 on Mo (HC-342)....		4.55×10^{-4}	.04	500	10:05	1.30
28B	TiB_2 on Inc. (HC-328)..	S	2.88×10^{-2}	.18	200	1:01	2.95×10^{-1}
28C	.....do.....	S	5.05×10^{-2}	.18	200	1:30	1.42×10^{-1}
29B	TiB_2 on Inc. (HC-329)..		2.00×10^{-2}	.18	200	2:34	2.31×10^{-1}
+30B	TiB_2 on Inc. (HC-330)..	S	2.21×10^{-3}	.05	500	2:08	1.21
+30C	.....do.....	S	1.92×10^{-3}	.04	500	10:59	5.22×10^{-1}
+31B	TiB_2 on Inc. (HC-331)..		2.33×10^{-4}	.04	500	10:08	1.70
32	Steel ball bearing.....		3.85×10^{-1}	.13	200	:40	1.20×10^{-1}
+33	.....do.....		4.75×10^{-4}	.05	200	2:03	1.93
34	Al_2O_3 single crystal...		1.07×10^{-2}	.13	200	1:01	5.79×10^{-1}
+35	.....do.....		5.04×10^{-4}	.03	200	6:52	1.03

[1]Disk material for all tests was 4150 steel (R_c~52).
[2]All wear tests run at 1,845 m/min.
[3]Orientation of pin was random except for tests 34 and 35, where α-axis was along normal [0001] direction.
[4]+ indicates lubricated wear test (SAE 30 oil).
[5]Inc. = Inconel.
[6]S indicates a sequential test.

Table 5 compares some of the low-speed and high-speed wear test results (all for unlubricated test conditions). These results show that for the same material combinations wear rates at high speed are generally lower than those at low speed. Also, the TiB_2 coatings with different substrates exhibit approximately the same wear rate at high speeds. In addition, at high speeds, the TiB_2 coatings exhibit better wear rates than steel ball bearings and are approaching the wear rates of Al_2O_3 single crystals.

TABLE 5. - Comparison of low- and high-speed wear tests with no lubrication

(Disks, 4150 steel, R_c~52)

Test	Pin[1]	Speed, m/min	Wear rate, $mm^3/kg-km$
3F	TiB_2 on Mo (HC-302)..	2.57	2.85×10^{-1}
7B	TiB_2 on Mo (HC-313)..	3.04	8.39×10^{-2}
24B	TiB_2 on Mo (HC-332)..	1,845	1.41×10^{-2}
5C	TiB_2 on Ni (HC-304)..	2.70	1.01×10^{-1}
21B	TiB_2 on Ni (HC-309)..	1,845	1.14×10^{-2}
28B	TiB_2 on In (HC-328)..	1,845	2.88×10^{-2}
12	Steel ball bearing...	2.01	8.32
32	.....do.....	1,845	3.85×10^{-1}
13	Al_2O_3 single crystal.	2.50	<.001
34	.....do.....	1,845	1.07×10^{-2}

[1]Individual coatings are labeled "HC-".

Table 6 provides a comparison of high-speed wear rate results for lubricated and unlubricated wear tests. As expected, the lubricated wear tests produce lower wear rates than the unlubricated wear tests. The TiB_2 coatings, under lubricated conditions, develop approximately the same wear rates (independent of substrate). This would indicate that the substrate material may not be an important factor in lubricated wear behavior. It also appears that the TiB_2 coatings are not as wear resistant as either the steel ball bearing or the Al_2O_3 single crystal under lubricated high-speed conditions. However, under unlubricated high-speed conditions, the TiB_2 coatings look promising compared to steel ball bearings and Al_2O_3 single crystals.

TABLE 6. - Summary of high-speed wear-test results

(Disks, 4150 steel, R_c~52)

Test	Pin[1]	Lubrication	Wear rate, $mm^3/kg-km$
21B	TiB_2 on Ni (HC-309)..	None.....	1.14×10^{-2}
22C	TiB_2 on Ni (HC-312)..	SAE 30 oil	2.20×10^{-3}
24B	TiB_2 on Mo (HC-332)..	None.....	1.41×10^{-2}
26B	TiB_2 on Mo (HC-338)..	SAE 30 oil	2.18×10^{-3}
28B	TiB_2 on Inc. (HC-328)	None.....	2.88×10^{-2}
30B	TiB_2 on Inc. (HC-330)	SAE 30 oil	2.21×10^{-3}
32	Steel ball bearing...	None.....	3.85×10^{-1}
33	.....do.....	SAE 30 oil	4.75×10^{-4}
34	Al_2O_3 single crystal.	None.....	1.07×10^{-2}
35	.....do.....	SAE 30 oil	5.04×10^{-4}

[1]Individual coatings are labeled "HC-".

Incremental Wear Test

Because of the rough nature of the TiB_2 coatings, particularly on molybdenum, a test was devised to run in the initial TiB_2-coated pins and to then conduct a modified (~1,800 m/min, high-speed) pin-on-disk wear test. This test sequence is termed an incremental wear test, and it was conducted according to the following steps.

1. Scanning electron micrographs of each pin in the as-prepared condition.

2. An initial run in on the modified pin-on-disk wear-test apparatus (that is, a modified grinding machine) to establish a wear flat approximately 0.10 cm in diameter (equivalent to a coating penetration of ≈ 51 μm on a 0.32-cm radius hemisphere).

3. SEM micrographs of each pin in the "run-in" condition.

4. A continuation of the wear test from the condition of run-in. Each pin is worn to produce a flat of ≈ 0.18 cm diameter (equivalent to a coating penetration of ≈ 130 μm beyond the run-in condition).

5. Calculation of the volume removed between "run-in" and the termination of the wear test (ΔV). Computation of wear rate, WR, from equation 3.

6. SEM micrographs of the worn flat at the end of the wear test.

The pins used for the incremental wear test were all molybdenum substrates and were specially prepared with thick TiB_2 coatings, as listed in table 7.

TABLE 7. - Molybdenum pins and approximate coating thickness

Test	Pin	Maximum coating thickness, μm	Minimum coating thickness at end of test, μm
36	HC-375	168	51
37	HC-376	218	66
38	HC-377	226	69
39	HC-378	221	81
40	HC-379	236	81
41	HC-380	211	86

The results of the high-speed incremental wear tests are listed in table 8. The average value for the wear rates shown in table 8 is 5.1×10^{-2} $mm^3/kg\text{-}km$, which is approximately the same as the wear rate for the nonincremental test, 1.41×10^{-2} $mm^3/kg\text{-}km$ (test 24B, table 4) given previously.

TABLE 8. - Results of high-speed pin-on-disk incremental wear tests[1]

(Disks, 4150 steel, R_c ~52)

Test	Pin[2]	Wear rate, mm^3, kg-km	Friction coefficient	Load, g	Time of test, min:sec	Final contact pressure, kg/mm^2	Comments
36A	HC-375	ND	ND	ND	ND	ND	SEM in as received condition.
36B	HC-375	ND	ND	200	ND	ND	SEM of run in.
36C	HC-375	6.42×10^{-2}	0.29	700	1:23	0.308	SEM after wear test.
36D	HC-375	ND	ND	ND	ND	ND	SEM of microhardness tests.
37A	HC-376	ND	ND	ND	ND	ND	SEM in as received condition.
37B	HC-376	ND	ND	200	ND	ND	SEM of run in.
37C	HC-376	5.38×10^{-2}	.30	700	2:47	.211	SEM after wear test.
37D	HC-376	ND	ND	ND	ND	ND	SEM of microhardness test.
38A	HC-377	ND	ND	ND	ND	ND	SEM in as received condition.
38B	HC-377	ND	ND	200	ND	ND	SEM of run in.
38C	HC-377	7.12×10^{-2}	.29	700	2:32	.211	SEM after wear test.
38D	HC-377	ND	ND	ND	ND	ND	SEM of microhardness test.
39A	HC-378	ND	ND	ND	ND	ND	SEM in as received condition.
39B	HC-378	ND	ND	200	ND	ND	SEM of run in.
39C	HC-378	4.77×10^{-2}	.29	700	3:01	.240	SEM after wear test.
39D	HC-378	ND	ND	ND	ND	ND	SEM of microhardness test.
40A	HC-379	ND	ND	ND	ND	ND	SEM in as received condition.
40B	HC-379	ND	ND	200	ND	ND	SEM of run in.
40C	HC-379	4.78×10^{-2}	.29	700	4:01	.206	SEM after wear test.
40D	HC-379	ND	ND	ND	ND	ND	SEM of microhardness test.
41A	HC-380	ND	ND	ND	ND	ND	SEM in as received condition.
41B	HC-380	ND	ND	200	ND	ND	SEM of run in.
41C	HC-380	2.30×10^{-2}	.29	700	5:00	.267	SEM after wear test.
41D	HC-380	ND	ND	ND	ND	ND	SEM of microhardness test.

ND Not determined.

[1]All wear testing at 1,843 m/min sliding speed and no lubricant.

[2]All TiB_2 coatings (the pins) on molybdenum.

From the incremental tests, it can be concluded that the effect of run-in does not alter the wear behavior of TiB_2 coatings on Mo substrates. This suggests that the previous results (tables 1 and 2) are probably representative of TiB_2 wear behavior, even though typical coatings had some porosity, and that the effect of air spaces does not seem to be significant.

Microhardness Tests

The six pins that were used in the incremental wear test, along with 11 other pins that were previously wear tested, were used as samples for hardness testing. The approximate coating thickness on the six incremental wear test pins are given in table 7. The approximate coating thickness for the 11 other test pins is listed in table 9. The numbers given in these two tables for the minimum coating thickness (dimension "X" in figure 3) remaining after the wear test were determined as follows (refer to fig. 3). Since the known original coating thickness, τ, is given by

$$\tau = X + h \tag{4}$$

and, from figure 3,

$$h = R_o - Z_o \tag{5}$$

then

$$X = \tau + Z_o - R_o \tag{6}$$

Substitution for R_o from equation 2 yields the result

$$X = \tau - R_o + \sqrt{R_o^2 - \left(\frac{d}{2}\right)^2} \tag{7}$$

TABLE 9. - Pins and approximate coating thickness for microhardness testing

Test	Pin	Maximum coating thickness, μm	Minimum coating thickness at end of test, μm
7B	HC-313	178	([1])
17B	Ni-4	([2])	NAp
18B	Mo-5	([2])	NAp
20C	HC-307	53	2
21B	HC-309	63	36
22C	HC-312	58	28
24B	HC-332	79	23
26C	HC-338	81	30
27B	HC-342	188	165
29B	HC-329	104	61
31B	HC-331	23	8

NAp Not applicable.
[1]Substrate penetrated.
[2]No coating.

It is important to note that all wear flats are assumed to be circular when applying the procedure outlined with figure 3. This assumption was generally true, as was later verified by SEM micrographs of various wear flats.

To evaluate the microhardness of the TiB_2 coatings, it is desirable to have a crack-free indentation, with a depth of penetration less than 10 pct of the minimum coating thickness, and with an indentation diagonal no smaller than 20 μm (a machine readability limitation). Ideally, a Knoop (elongated diagonal) indentor would be used for this type of work. Because of the roughness of the wear flat surfaces, it was impossible to obtain high-quality Knoop impressions. Thus out of necessity, a Vickers (symmetrical indentor, 136° included angle between faces) indentor was used with an applied load of 500 g.

The results obtained from microhardness testing (all microhardness testing was done after the wear tests were completed) for the incremental wear-test pins and the 11 other wear pins are given in tables 10 and 11. The test numbers (for example, 21, 22, 31, etc.) correspond to the pins used in the wear tests reported in tables 1 and 4, but the specific numbers (21C, 22D, 31C) are not entered in tables 1 and 4, as these numbers refer to the microhardness tests. The location numbers given in tables 10 and 11 simply refer to random locations on the wear flat surface. These locations were later observed in the SEM, and some of these micrographs are shown in this section.

TABLE 10. - Results of microhardness testing of incremental wear-test pins

Test	Pin	Location	Hardness,[1] kg/mm^2	Comments
36D	HC-375	1	2,770	Good indentation.
		3	2,440	Coating flaking.
		4	[2]1,540	Good indentation.
37D	HC-376	1	2,620	Good indentation.
		2	2,540	Do.
		3	2,270	Coating cracking.
		4	1,440	Good indentation.
38D	HC-377	1	2,890	Good indentation.
		2	2,740	Do.
39D	HC-378	1	2,710	Good indentation.
		2	1,830	Some coating cracking.
40D	HC-379	1	2,360	Good indentation.
		2	2,360	Some cracking.
41D	HC-380	1	2,740	Good indentation.
		2	2,800	Some cracking.

[1]All numbers are Vickers microhardness (obtained using a 500-g indenting load on a Tukon microhardness machine), unless otherwise noted.

[2]Knoop hardness number (using a 500-g indenting load).

TABLE 11. - Results of microhardness testing of miscellaneous wear-test pins

Test	Pin	Location	Hardness,[1] kg/mm^2	Comments
7C	HC-313	1	2,140	Small indentation, some cracking.
		2	2,600	Do.
17C	Ni-4	1	458	Ni substrate--no coating.
		2	466	Do.
18C	Mo-5	1	247	Mo substrate--no coating.
		2	250	Do.
20D	HC-307	1	222	Coating worn away.
		2	285	Do.
21C	HC-309	1	2,140	Small indentation, no cracking.
		2	2,020	Do.
22D	HC-312	1	179	Coating worn away.
		2	196	Do.
24C	HC-332	1	2,210	Deep cracking.
		2	[2]2,170	Do.
26D	HC-338	1	2,830	Do.
		2	3,250	Do.
27C	HC-342	1	3,690	Mild cracking.
		2	3,100	Do.
29C	HC-329	1	2,270	Small indentation, no cracking.
		2	2,210	Do.
31C	HC-331	1	5,240	Do.
		2	4,350	Do.

[1]All numbers are Vickers microhardness (obtained using a 500-g indenting load on a Tukon microhardness machine), unless otherwise noted.
[2]Vickers microhardness (300-g indenting load).

For the Vickers indentor geometry, it can be shown that a diagonal length of 20 μm corresponds to a penetration depth of 2.8 μm or a hardness value of 2,360 kg/mm^2 (with an applied load of 500 g). This means that for all Vickers hardness numbers greater than 2,360 kg/mm^2, the depth of the indentation is 2.8 μm or less. Since most minimum coating thickness values were 28 μm or greater, it is relatively safe to assume that the influence of the substrate was minimal. For those cases where the coating thickness was not sufficiently great, the resultant microhardness number would be expected to be smaller than for just the coating by itself, since the substrates Ni, Mo, and Inconel are softer than TiB_2.

Shown in figure 4 is a typical indentation hardness mark (test 41D) for a Mo substrate; the hardness is 2,740 kg/mm^2. The minimum coating thickness for this pin is 86 μm (see table 7). Note that the indentation mark is extremely symmetrical, indicating that the surface is very flat and perpendicular to the indentor at this location. The average length of the two indentor diagonals is 19.8 μm, giving a coating penetration of 2.8 μm. For this pin, the indentation depth is only 3 pct of the minimum coating thickness--thus no substrate effect is present. It is typical of most of these indentations that a crack forms at the corner of the diagonal, as is shown in figure 4. The

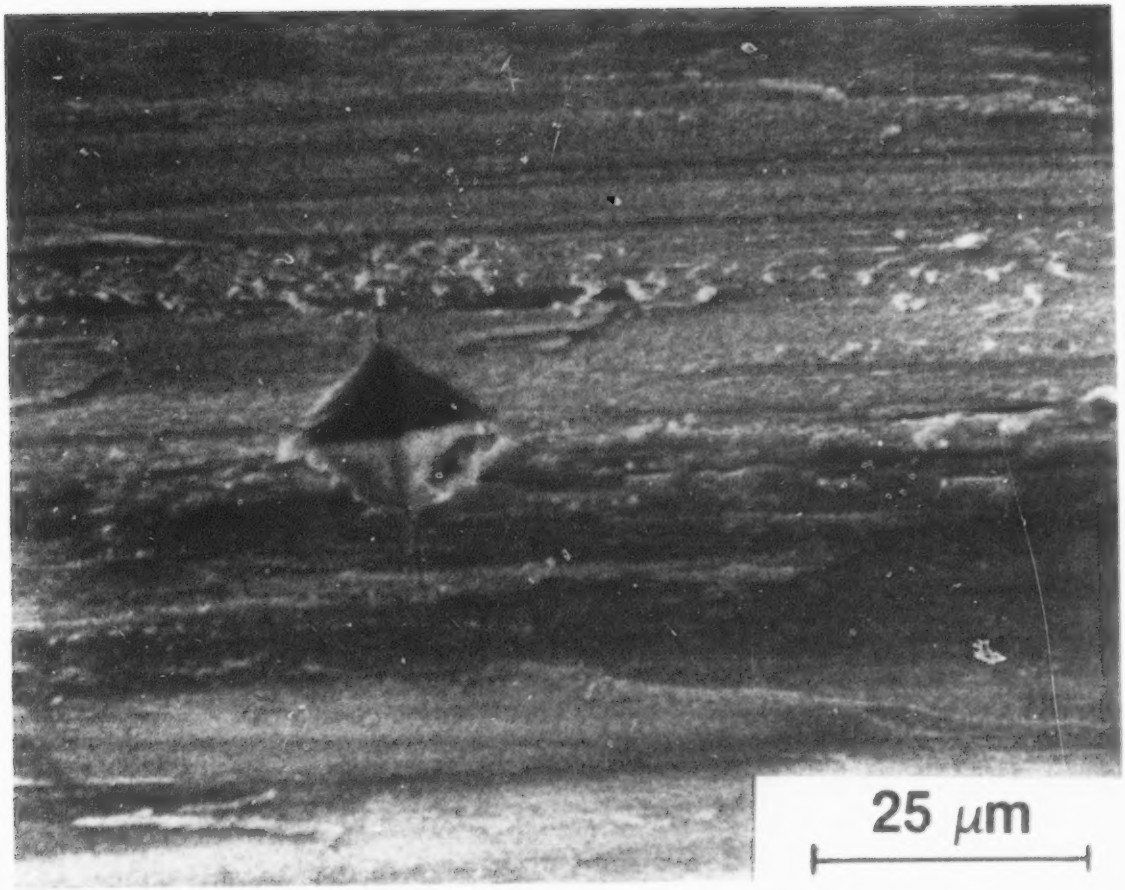


FIGURE 4. - Microhardness indentation on test pin 41 (molybdenum substrate). Hardness, 2,740 kg/mm^2, tilt 5°.

presence of the crack would probably make the indentation marker larger than that for an uncracked case, and thus the resulting microhardness number is lower than that of an uncracked case.

An example of an indentation mark that shows no cracks is shown in figure 5 (Inconel substrate; the hardness at this location is 5,240 kg/mm^2. The minimum coating thickness for this pin is 7.6 μm. The average length of the two indentor diagonals is 14 μm, giving a coating penetration of 2.0 μm. Thus, the indentation depth is approximately 25 pct of the minimum coating thickness. For this particular wear flat, SEM micrographs showed that the location of this indentation was closer to the outside of the wear flat (thus, larger coating thickness) than the center (where the minimum coating thickness is computed). Even with this consideration, which we interpret as meaning there may be a slight substrate effect, it is remarkable that the hardness is 5,240 kg/mm^2.

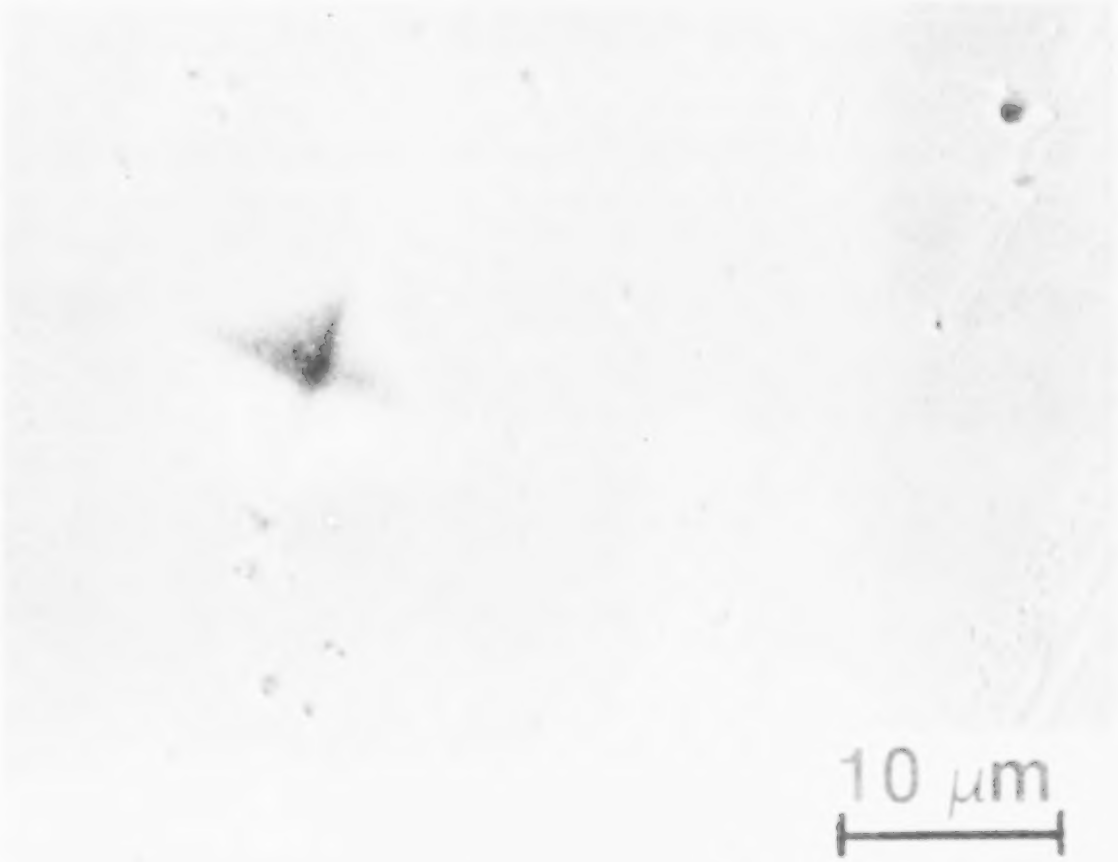


FIGURE 5. - Microhardness indentation on test pin 31 (Inconel substrate). Hardness, 5,240 kg/mm^2, tilt 0°.

Based upon the microhardness results reported in this section, it appears that TiB_2 microhardness values go from a high of 5,240 kg/mm^2 (with no cracking) to values of approximately 2,200 kg/mm^2 (with various amounts of cracking). It seems reasonable to conclude that the best TiB_2 coatings are probably much harder than Al_2O_3 (typical Vickers 500-g microhardness of 2,000 to 3,000 kg/mm^2), but exactly how much harder cannot be stated at this time.

Scanning Electron Microscopy

In general, the surface appearance of TiB_2 coatings (unworn) on both nickel and Inconel substrates can be characterized as uniform and fairly smooth. Examples of these two surfaces are shown in the micrographs of figures 6 and 7. The general surface appearance of TiB_2 coatings (unworn) on molybdenum substrates can be characterized as uniform and rough, with a large number of round particles making up the coating. An example of this type of surface is shown in figure 8.

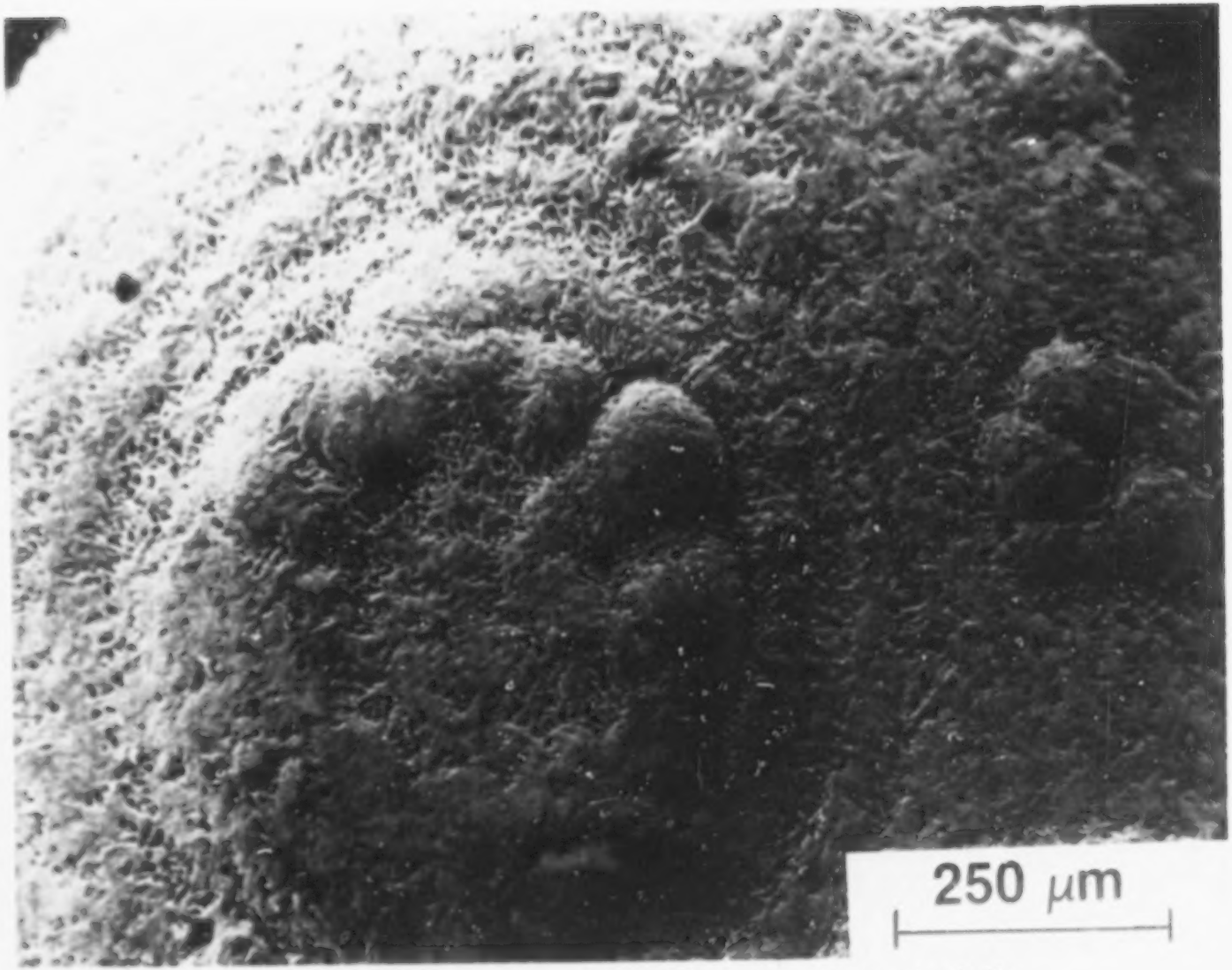


FIGURE 6. - TiB_2 coating (unworn) on nickel substrate. Test pin 5, tilt 20°.

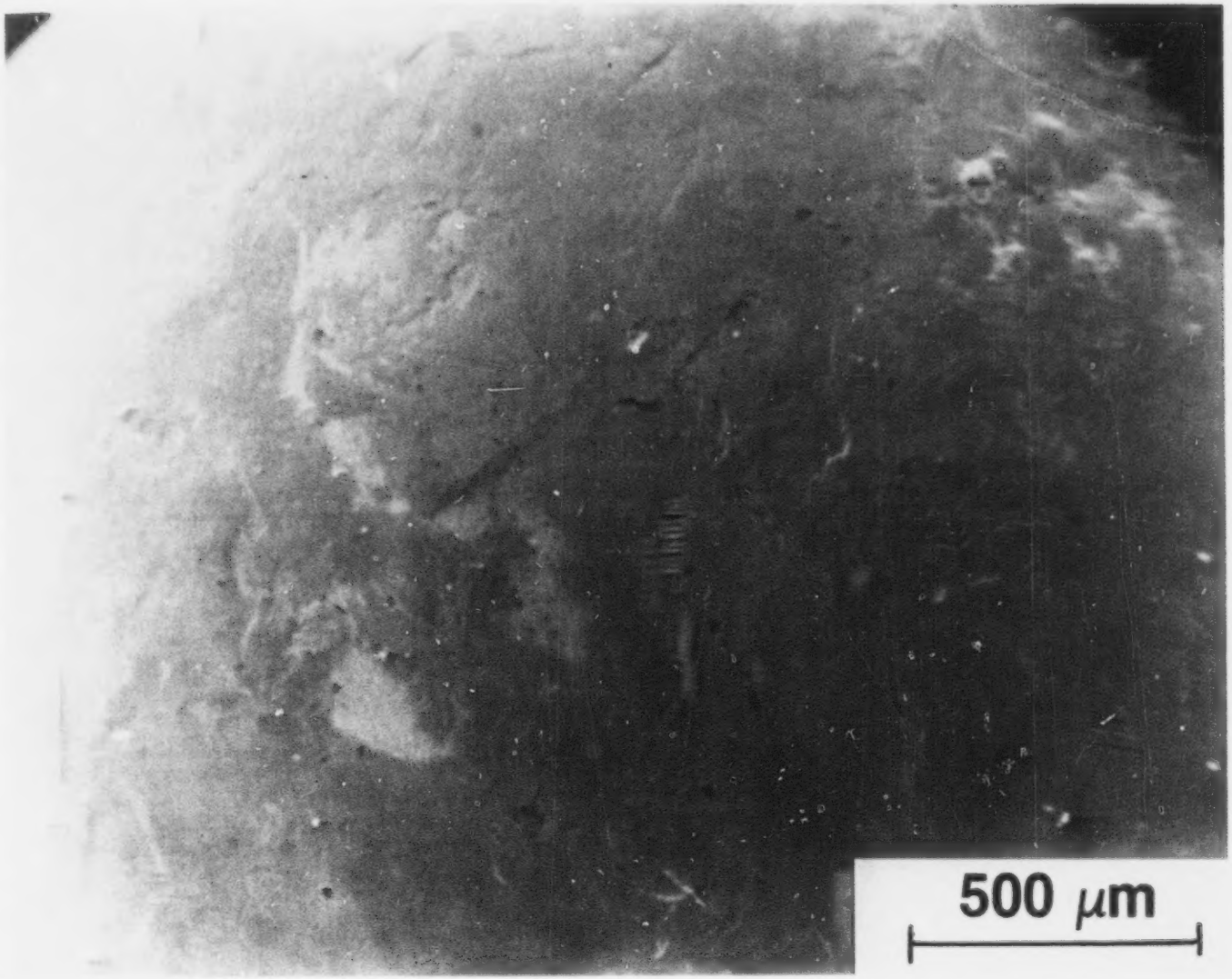


FIGURE 7. - TiB_2 coating (unworn) on Inconel substrate. Test pin 28, tilt 0°.

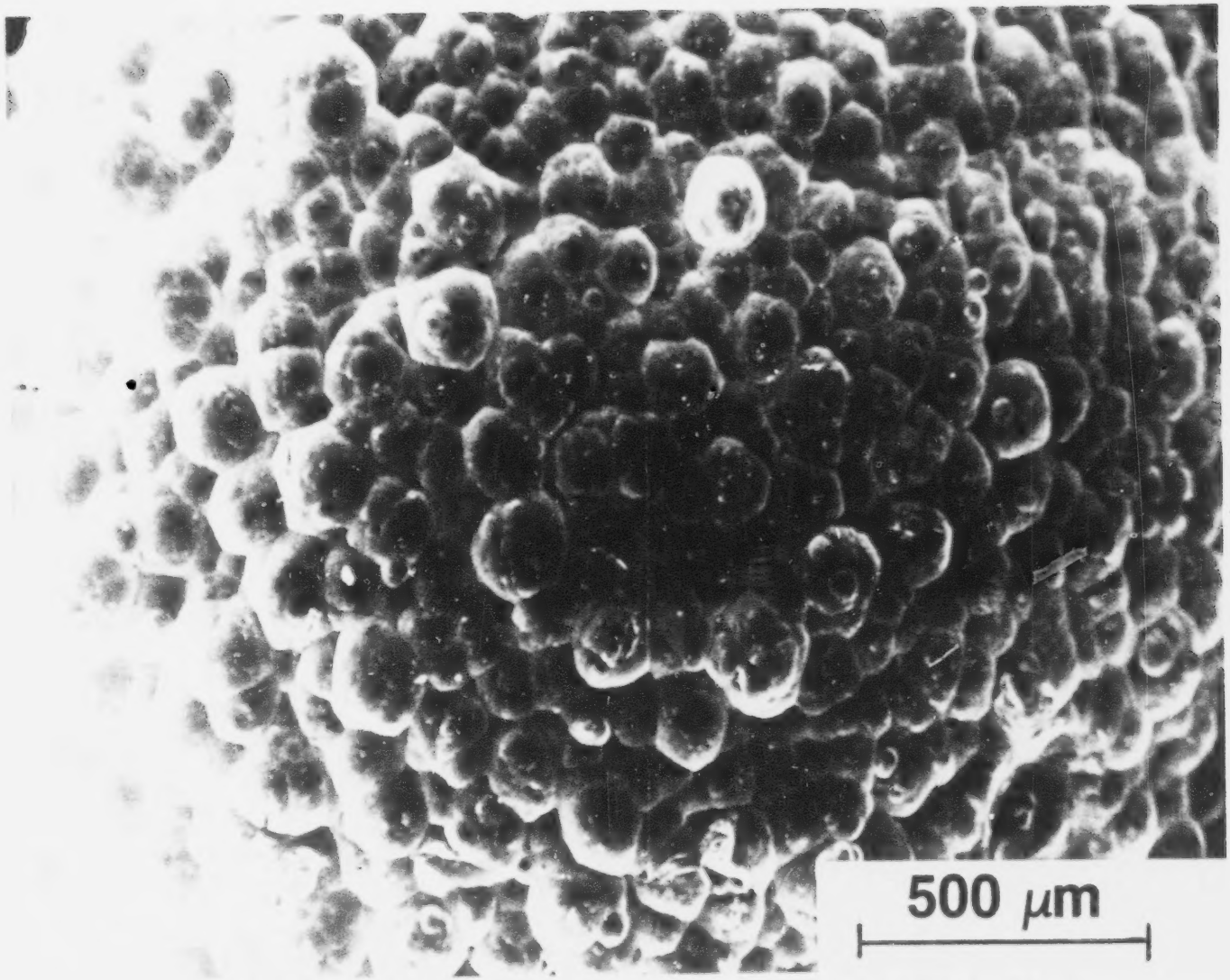


FIGURE 8. - TiB_2 coating (unworn) on molybdenum substrate. Test pin 40, tilt 0°.

One purpose of the incremental wear test was to evaluate TiB_2 coatings on molybdenum substrates. Based on figure 8 it appears that the actual wear flat is composed of spherical TiB_2 contacts with air voids between them. If a wear evaluation (that is, determination of the volume of removed material) was based on the outer diameter of the overall wear flat, the amount of TiB_2 lost owing to wear would be overestimated. The results of the incremental wear test, however, showed that this problem was not present.

The low-speed wear-test surfaces (unlubricated, against 4150 steel) generally look very smooth, with the wear process appearing to polish the TiB_2 coating (indicative of adhesive wear; that is, small-scale particle transfer between TiB_2 and 4150 steel (4)). There was no appearance of gross coating dislodgment, indicating that coating-substrate bonding failure is not an important wear mechanism.

Figures 9 and 10 are micrographs of a sequential low-speed unlubricated wear test (test 6). For these and all other SEM micrographs, the leading edge

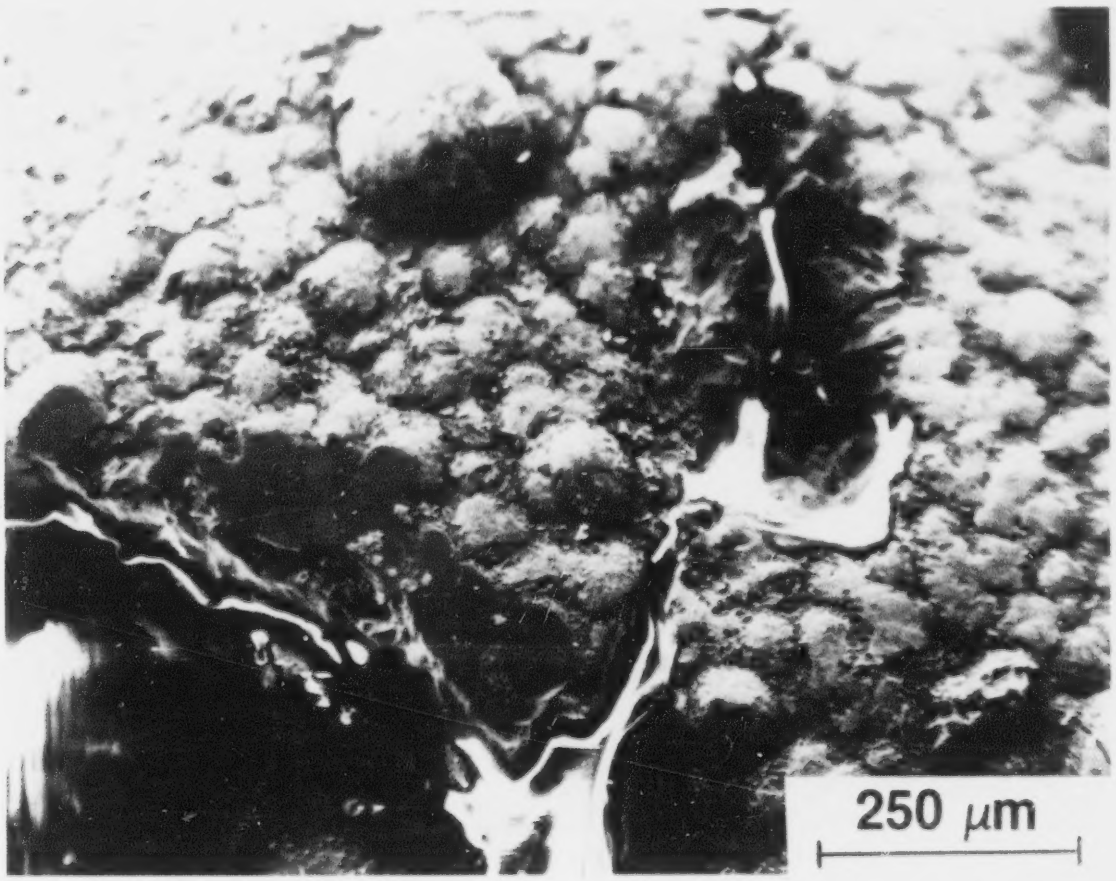


FIGURE 9. - TiB_2 coating on molybdenum substrate, showing smooth, polished surface early in the wear test. Test 6C, tilt 20°.

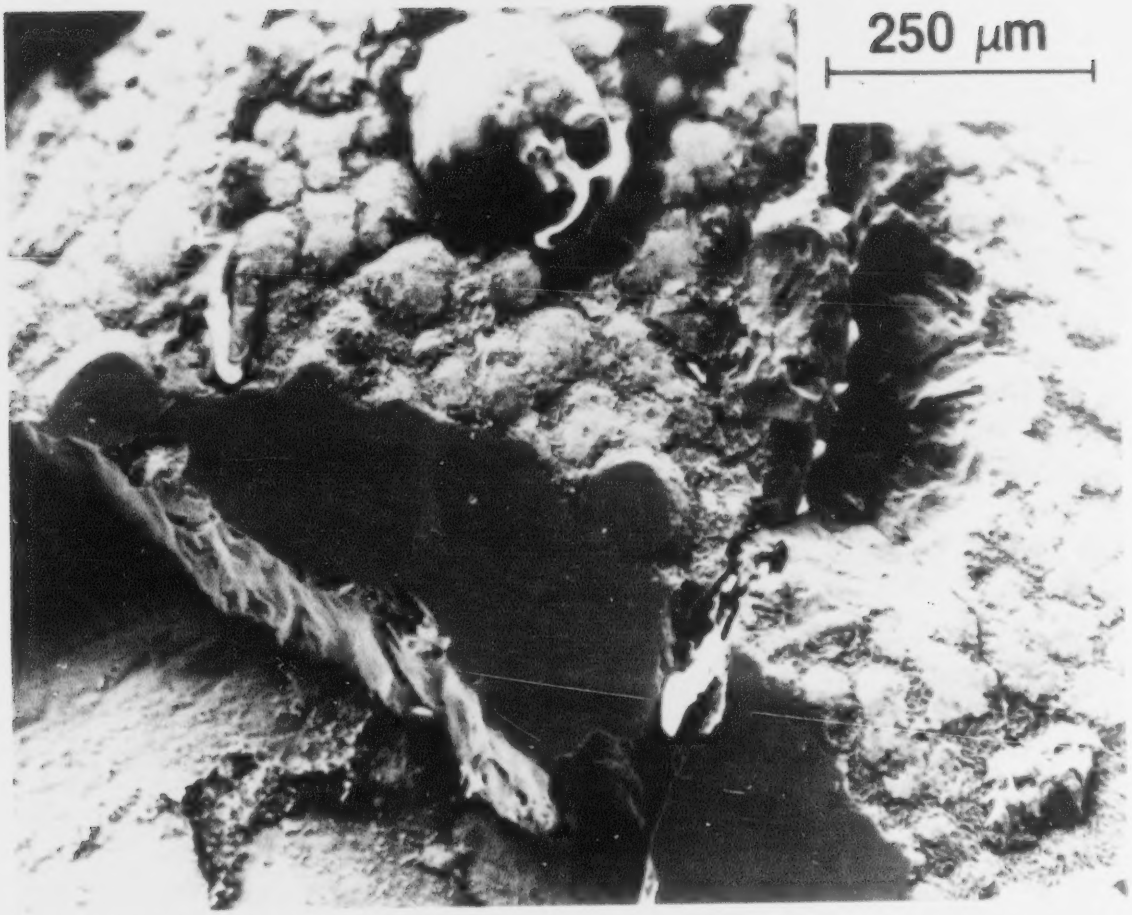


FIGURE 10. - TiB_2 coating on molybdenum substrate, showing smooth, polished wear surface at end of test. Test 6D, tilt 20°.

of the flat is to the left of the micrograph. Figure 9 shows that the TiB_2 surface is quite smooth and polished owing to the sliding wear. With continued testing (fig. 10), the surface appears to wear larger and remains quite smooth. Note that the hole in the coating was present at the start of testing and is not the result of wear testing.

The adherence between coating and substrate has generally proven to be quite good. Figure 11 is a micrograph of complete coating penetration showing the exposed Inconel substrate (light area) beneath the coating. Penetration of this coating was confirmed by scanning electron microscopy X-ray mapping techniques. The excellence of coating adherence is shown by the cleanly defined edge line between coating and substrate. This line was very well defined around the wear flat, and there was no noticeable coating chipping (or flaking) anywhere along this line. The noncircular wear track is due to the

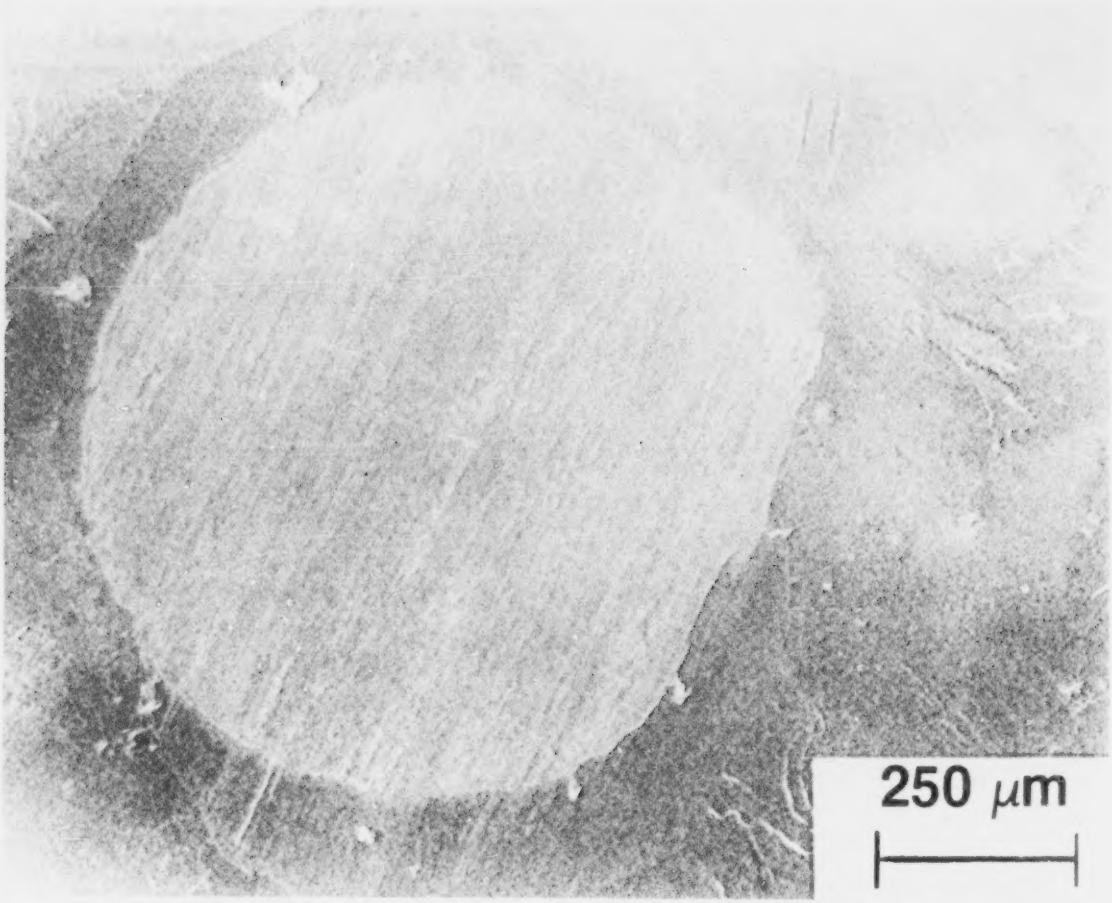


FIGURE 11. - TiB_2 coating on Inconel substrate at the end of high-speed unlubricated wear test. The lighter, circular area is the substrate and the leading edge of the pin is to the upper right. Test 28C, tilt 0°.

very nonuniform coating thickness on this sample. No similar variation in coating thickness was observed on other wear tests.

At high speeds with no lubrication, the wear surfaces of TiB_2 generally look smooth, as shown in figure 12. The smooth type of wear surface was not dependent on the type of substrate and appeared the same for Mo, Ni, and Inconel substrates. In general, the high-speed wear surfaces look similar to those observed under low-speed wear-test conditions. It is therefore postulated that the wear mechanisms are similar at both low and high speeds under unlubricated conditions. It also appears that the type of substrate does not influence the wear rates (see table 5). The fact that the wear rates are higher at low speed would indicate that, although the wear mechanisms may be similar (at low and high speeds), there is a speed effect on wear. This speed effect may be due to interface temperatures, as they are surely higher in the

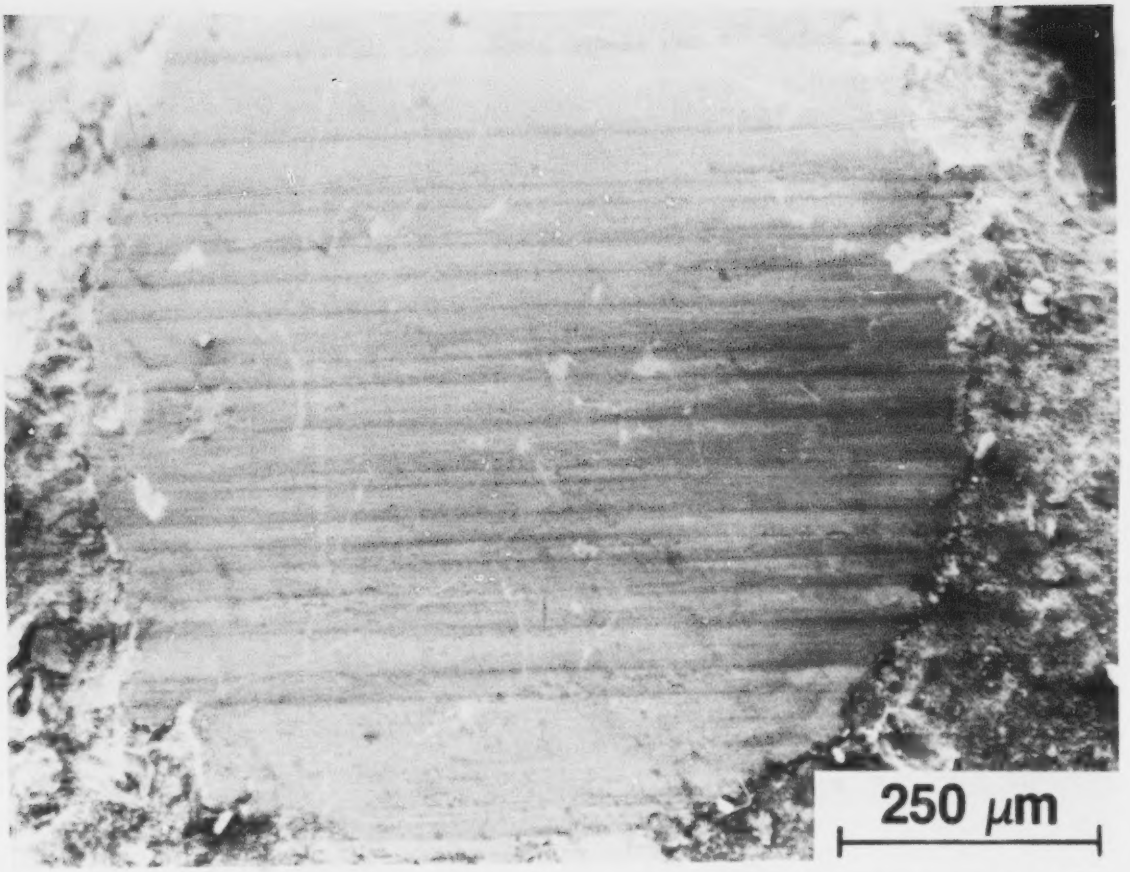


FIGURE 12. - TiB_2 coating on molybdenum substrate, with smooth wear flat at end of high-speed unlubricated wear test. Test 24B, tilt 20°.

high-speed wear-test. This suggests that TiB_2 may wear better in harsher test environments.

At high speeds (with lubrication) the wear surfaces show a pronounced microchipping wear in addition to the smooth type of wear flats shown previously. Microchipping wear is shown in figure 13 for a TiB_2 coating on a nickel substrate. This type of wear surface is characterized by a wear flat that contains a significant fraction of craters on the flat surface. Looking inside of these craters shows numerous fracture marks, indicating that the entire crater may have been formed when a section of TiB_2 spalled from the flat surface. Microchipping wear was observed only under lubricated high-speed wear conditions and only for TiB_2 on Ni (test 22) and Mo (test 26) substrates. It was not observed for TiB_2 on Inconel (test 30), most probably because the coating was quite thin on this pin and was penetrated during the wear test. It should be noted that microchipping wear has also been observed by Kirk (3) in lubricated grinding and high-speed lubricated pin-on-disk testing of Al_2O_3 against steel. It is suggested that this type of wear mechanism

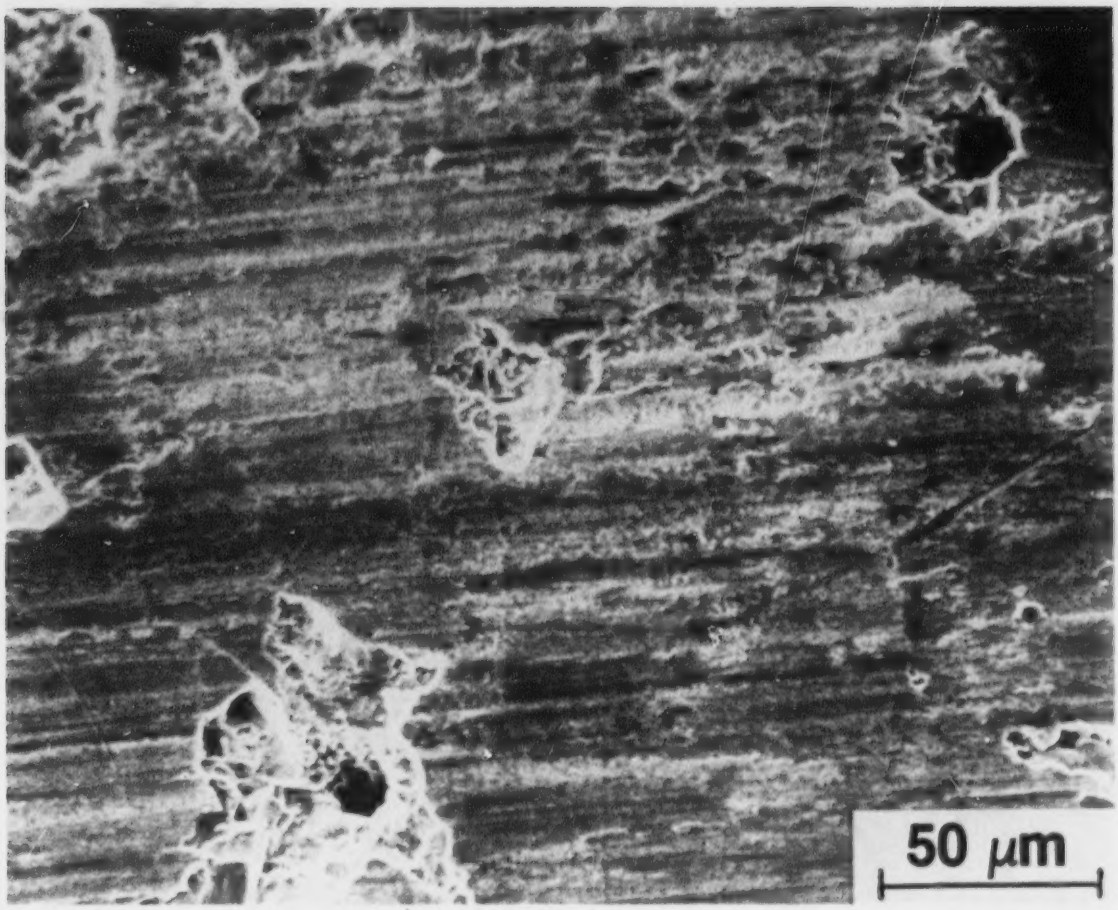


FIGURE 13. - TiB_2 coating on nickel substrate at the end of lubricated wear test, showing microchipping wear characterized by fracture pockets on the wear flat. Test 22B, tilt 20°.

is predominant only under lubricated wear when one of the sliding members is a very hard and brittle material. However, no totally convincing explanation of why microchipping wear occurs can be offered at this time.

The results of SEM micrographs for the incremental wear test program (all on molybdenum substrates) did not show any new features not previously seen. In general, the run in wear flat was characterized by smooth wear of TiB_2 round particles (see figure 8 for typical unworn TiB_2 on a molybdenum surface). Continuation of the wear test resulted in an enlargement of the wear flat with the overall smooth wear surface persisting. Although there were some fracture pockets on the final wear flat (similar to the craters shown in figure 13), they were believed to be the result of exposing voids in the coating and of small-scale fracture of the TiB_2 coating. These coatings do not occupy a significant portion of the overall area of wear flat.

SUMMARY

The newly developed chemical conditioning technique has been shown to require much less time to prepare TiB_2 plating baths than the electrochemical procedure used previously.

Both the low-speed and high-speed wear-test results have shown that the TiB_2 wear rates are generally independent of the type of substrate. The low-speed unlubricated sliding wear rates for TiB_2 coatings against 4150 steel were shown to be comparable to the wear rates for the uncoated nickel and molybdenum substrate materials and exhibited much higher low-speed wear rates than those measured for Al_2O_3 single crystals. Wear rates of TiB_2 are lower at high speeds (table 5), suggesting that TiB_2 coatings will perform better in harsher sliding environments. In addition, an incremental wear test has been developed to show that the effect of run-in (to produce an initial wear flat) is not significant in improving the wear rates of TiB_2 coatings.

Scanning electron micrographs have shown there is excellent adhesion between TiB_2 and each of the three (Mo, Ni, and Inconel) substrates. The wear surface morphology under unlubricated wear conditions was seen to be similar at both low and high speeds. These surfaces were generally very smooth wear flats, indicative of the slow removal of material from the TiB_2 surface.

Scanning electron micrographs have been useful in identifying microchipping wear of TiB_2 coatings in high-speed lubricated wear tests. This type of wear leaves sharp-edged pockets (or craters) in the TiB_2 surface.

Microhardness measurements indicate that TiB_2 is an extremely hard material, with a hardness of greater than 5,200 kg/mm^2 observed in one measurement. However, the material is subject to cracking during the microhardness tests, resulting in a lower apparent hardness. The best TiB_2 coatings appear to be much harder than Al_2O_3.

The TiB_2 coatings appear to be most comparable to Al_2O_3 (the standard used for comparison) in high-speed unlubricated sliding wear tests. This would appear to be the best area to look at for applications.

REFERENCES

1. Duwell, E. G. Friction and Wear of Single-Crystal Sapphire Sliding on Steel. Wear, v. 9, 1966, pp. 363-368.

2. Flinn, D. R., F. X. McCawley, G. R. Smith, and P. B. Needham, Jr. Electrodeposition of Erosion-Resistant Titanium Diboride Coatings. BuMines RI 8332, 1979, 29 pp.

3. Kirk, J. A. Fundamental Studies of Grinding Performance-Lubricated Grinding. Final Report to National Science Foundation (Rept. UMME-GR-01), January 1976.

4. Rabinowicz, E. Friction and Wear of Materials. John Wiley & Sons, Inc., New York, 1965, pp. 104-124.

5. Schlain, D., F. X. McCawley, and G. R. Smith. Electrodeposition of Titanium Diboride Coatings. BuMines RI 8146, 1976, 22 pp.

6. Steijn, R. P. On the Wear of Sapphire. J. Appl. Phys., v. 32, 1961, pp. 1951-1958.

7. Zum Gaur, K. H. How Microstructure Affects Abrasive Wear Resistance. Metal Prog., v. 116, 1979, pp. 46-52.

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INT.-BU.OF MINES,PGH.,PA. 25331